

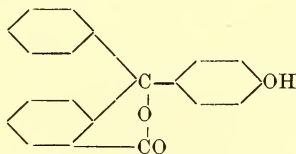
COLOUR AND CHEMICAL CONSTITUTION: A STUDY OF THE PHTHALEINS AND RELATED COMPOUNDS.

By JAMES MOIR, M.A., D.Sc., F.I.C.

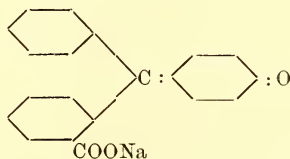
Whilst it has been known for a long time that if a coloured organic substance or dye is converted into a substitution product (*e. g.* aurine into eupittonic acid), the colour is much deepened, yet there are remarkably few systematic researches on record which give any clue as to the factors governing this phenomenon, important as it is from the practical point of view. Of the recorded work practically all belongs to the azo-dye series—for example, J. T. Hewitt's investigation into the changes of colour produced in nitrobenzeneazo-*a*-naphthol by adding the sulphonic group to its molecule in the different possible positions; also the recent interesting and systematic work emanating from the Dacca College, India.

The present paper purports to be, as far as possible, a complete study of the phthaleins and of other derivatives of the parent substance fuchson, and the work has consisted, briefly, in an examination of the colour and absorption-spectrum of every phthalein and oxy- derivative of triphenylcarbinol that could be made with the materials at my disposal, and of an attempt to include all the numerous and puzzling data in a comprehensive theory of colour-change.

The simplest phthalein possible is monoxydiphenylphthalide (also known as phenylphenolphthalein, and in Germany incorrectly as "benzolphenolphthalein"), a colourless substance usually depicted by the formula

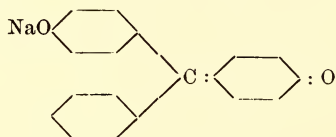


which, when dissolved in alkali, becomes coloured (a rather purplish pink), and is then assumed to have been converted into the quinonoid form :

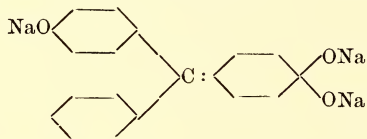


As will be seen from the latter formula, the substance is the ortho-carboxylic acid of fuchsone, the latter being the inner-anhydride of para-oxy-triphenylcarbinol, and its systematic name being diphenyl-methylenequinone ("diphenyl-chinomethan" in Germany). The centre of its absorption band lies at about λ 560 (frequency 17·86). Fuchsone itself cannot be investigated by this method, since it is a neutral body giving no colour in alkali, though itself coloured (orange).

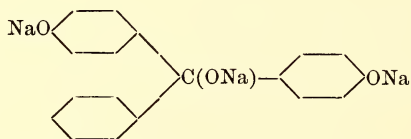
Another related compound of simple constitution may be taken next, although it is not a phthalein—viz. benzaurine or 4'-oxyfuchsone



This differs chemically from the preceding compound in having no ortho- CO_2Na group, but has a para-ONa group instead (both phenyl groups of the fuchsone molecule having the same function). This alkaline group confers solubility in water, with colour, as in the foregoing case, but the colour is now a reddish-purple with absorption-band at λ 570 (frequency 17·55). The addition of strong NaOH to benzaurine first deepens the colour to purple (absorption-band λ 585), probably due to the formation of



and, on warming, bleaches the colour owing to the destruction of the quinonoid ring to form



or the trisodium salt of dioxytriphenylcarbinol, by migration of an $-\text{ONa}$ group from the end to the middle of the system. The same behaviour is shown by monoxydiphenylphthalide in an exaggerated degree, only a slight alkalinity sufficing to bleach it.

The effect of the addition of a second para-OH (or $-\text{ONa}$) group to the molecule may next be studied. Ordinary phenolphthalein is the para-OH derivative of monoxydiphenylphthalide, and ordinary aurine is the corresponding OH derivative of benzaurine. The effect is surprising, since in both cases the absorption-band moves down the spectrum into the green,

phenolphthalein having its band at $\lambda 554$ (frequency 18.05), and aurine having its band at $\lambda 530$ (frequency 18.88). In the former case the change caused by the extra $-\text{OH}$ group is insignificant, the frequency having only risen by 0.2; but in the case of aurine the difference is very great, the frequency being raised by 1.6 or nearly 10 per cent. This abnormal behaviour of aurine is doubtless connected with its almost perfect chemical symmetry as compared with all the other compounds which I deal with: as anhydride of $\text{C}(\text{OH})(\text{C}_6\text{H}_4\text{OH})_3$, it has always three paths by which it may become quinonoid in the form $\text{C}(\text{C}_6\text{H}_4\text{O})_3\text{H}_2$. It may be noted that concentrated alkali raises the band of aurine to $\lambda 539$.

Again, phenolphthalein may be looked on as the *o*-carboxylic acid of benzaurine, whence we infer that this $-\text{CO}_2\text{H}$ group causes a change of frequency of 18.05–17.55 or 0.5, from which the theoretical frequency of the parent substance fuchsone can be deduced to be about 17.3—viz. that of monoxydiphenylphthalide less 0.5. Thus, the passage from fuchsone to oxyfuchsone (benzaurine), with destruction of the symmetry, involves a rise of only 0.2 in the frequency, whereas the entrance of a second OH group, giving aurine and restoring the symmetry, leads to a rise of 1.6 in the frequency. This theoretical figure for alkaline fuchsone is confirmed by the fact that it gives a frequency of 22.0 when dissolved in H_2SO_4 ; this is 1.4 above the value for monoxydiphenylphthalide, and benzaurine is found to give a frequency in H_2SO_4 , which is 1.5 above that of phenolphthalein.

To complete the series I have prepared a small quantity of the unknown aurine-*o*-carboxylic acid (which is also the 4'-oxy-derivative of phenolphthalein) by condensing 4'-oxyphthalic acid with phenol. It was found to give a pink solution in caustic alkali, possessing a band at $\lambda 542$, exactly half-way between those of aurine and phenolphthalein.

STUDY OF THE SUBSTITUTED PHENOLPHTHALEINS.

These were chosen for investigation on account of their easy synthesis rendering it possible to make a large number of derivatives; but it was also found that their absorption-bands are remarkably definite as a rule, thus rendering accurate measurements of their centres possible, which is generally not the case with the commoner dye-stuffs, particularly those of the azo-class which have been hitherto investigated. The centre of the band can generally be estimated within one unit of wave-length (in 10^{-9} metres) in the green, but with less accuracy at the red end; consequently the frequency values in Tables I and II can, as a rule, be trusted to within about 0.05 unit—*i. e.* to an extent considerably finer than that to which the eye can appreciate differences of shade of colour.

A set of 50 phthaleins has been prepared and examined, and the results are classified in two tables. Table I gives the results for the simple deriva-

TABLE I.
Colours and Spectra of Derivatives of Phenolphthalein in Alkaline Solution.

No.	Name.	Source.	Alkaline Colour.	Centre of Absorption Band $\lambda \times 10^7$ cm.	Frequency $\frac{1}{\lambda} \div 10^3$ per cm.	Diminution of Frequency.	Cause of Diminution.
1	Phenolphthalein	PA and phenol	Pink	554	18.05	—	—
2	Monomethylether of phenolphthalein	ABA and phenol	"	555	18.00	0.05	One <i>p</i> CH ₃ .
3	Methylsalicylatephenolphthalein	PA and wintergreen oil.	"	557	17.95	0.10	Two <i>o</i> -CO ₂ CH ₃ .
4	Phenol-3-oxyphtalein	3-oxyphtalic acid and phenol	"	557	17.95	0.10	One OH in phtalic ring.
5	Phenolphthalein - disulphonic acid	PA and phenol- <i>o</i> -sulphonic acid	"	557	17.95	0.10	Two <i>o</i> SO ₃ Na
6	Phenolphthalein - <i>o</i> -dicarboxylic acid	PA and salicylic acid	"	559	17.90	0.15	Two <i>o</i> -CO ₂ Na.
7	Phenolphthalein- <i>m</i> -dicarboxylic acid	PA and <i>m</i> -oxybenzoic acid	"	559	17.90	0.15	Two <i>m</i> -CO ₂ Na.
8	Phenolphenyphthalein	BBA and phenol	"	560	17.85	0.20	Absence of one <i>p</i> -OH.
9	<i>O</i> -cresolphenylphthalein	BBA and <i>o</i> -cresol	Purplish-pink	564	17.75	0.30	Do., with gain of one <i>o</i> -CH ₃ .
10	Phenoltetrabromophthalein	TBP and phenol	"	565	17.70	0.35	Four Br in phtalic ring.
11	Dibromophenolphenyphthalein	Bromination of No. 8	"	568	17.60	0.45	Two <i>o</i> -Br minus one <i>p</i> -OH.
12	<i>O</i> -cresolphthalein	PA and <i>o</i> -cresol	"	571	17.50	0.55	Two <i>o</i> -CH ₃ .
13	<i>O</i> -dibromo- <i>o</i> -cresolphthalein	Bromination of No. 12	Purple	578	17.30	0.75	Two <i>o</i> -CH ₃ plus two <i>o</i> -Br.
14	Tetrabromophenolphthalein	Bromination of No. 1	"	583	17.15	0.90	Four Br (ortho) in phenol rings.
15	Tetridophenolphthalein	Iodination of No. 1	Bluish-purple	586	17.05	1.00	Four I (ortho) in phenol rings.
16	Catecholphthalein (NaHCO ₃)	PA and pyrocatechol	"	586	17.05	1.00	Two <i>o</i> -OH (not ONa).
17	<i>M</i> -cresolphthalein	PA and metacresol	"	590	16.95	1.10	Two <i>m</i> -CH ₃ .
18	Thymolphthalein	PA and thymol	Blue	597	16.75	1.30	Two <i>m</i> -CH ₃ plus two <i>o</i> -C ₂ H ₅ .
19	<i>M</i> -chlorophenolphthalein	PA and <i>m</i> -chlorophenol	"	597	16.75	1.30	Two <i>m</i> -Cl.

20	Guaiacolphthalein	PA and guaiacol	Blue	599	16.70	1.35	Two o -OCH ₃ .
21	Carvacrophthalein	PA and carvacrol	"	601	16.65	1.40	Two o -CH ₃ plus two m -C ₃ H ₇ .
22	Tetrahydronaphtholphthalein 2.3 (butylenephenolphthalein)	PA and tetrahydronaphthol	Dichroic	602	16.60	1.45	Two o -(CH ₂) ₄ joined o and m .
23	Octobromophenolphthalein	Bromination of No. 10	Blue	608	16.45	1.60	Four Br in phthalic ring and two Br in each phenol ring (ortho).
24	Protocatechuicphthalein	PA and protocatechuic acid	"	612	16.35	1.70	Two o -OH plus two m -CO ₂ Na.
25	Thymoltetrabromophthalein	TBP and thymol	Greenish-blue	623	16.05	2.00	Four Br in phthalic ring, and two m -CH ₃ plus two o -C ₃ H ₇ .
26	Dibromocarvacrophthalein	Bromination of No. 21	"	623	16.05	2.00	Two o -Br, two o -CH ₃ , and two m -C ₃ H ₇ .
27	Dibromothymolphthalein	Bromination of No. 18	"	625	16.00	2.05	Two o -Br, two m -CH ₃ , and two o -C ₃ H ₇ .
28	O -diaminophenolphthalein	Reduction of dinitro-compound	"	630	15.90	2.15	Two o NH ₂ .
29	Catecholphthalein (NaOH)	As No. 16	Green	652	15.35	2.70	Two o -ONa (or orthoquinoid linkage).
30	α -naphtholphthalein	PA and α -naphthol	"	662	15.10	2.95	Two o -CH:CH:CH:CH-
31	α -naphthol-3-oxypthalein	From 3 oxypthalein acid	"	662	15.10	2.95	No apparent change for this OH.
32	Dibromoguaiacolphthalein	Bromination of No. 20	Dichroic	673	14.85	3.2	Abnormally high.
33	α -naphtholtetrabromophthalein	TBP and naphthol	Yellow-green	678	14.75	3.3	Naphthalene rings and four Br.
34	α -naphtholphenylphthalein	BBA and naphthol	Greenish-yellow	About 720	13.9 (?)	4.2 (?)	One naphthalene ring; absence of one OH.
35	Dibromocatecholphthalein	Bromination of No. 16	Dirty purple	About 720	13.9 (?)	4.2 (?)	(Second band λ 489.)
36	o -dinitrophenolphthalein	Nitration of No. 1	Yellow	Off the	visible	spectrum	Two o -NO ₂ .
37	m -dinitrophenolphthalein	PA and m -nitrophenol	Brown	"	"	"	Two m -NO ₂ .
38	Resorcinolphenyolphthalein	BBA and resorcinol	Orange	"	"	"	Remarkable isomer of phenolphthalein.
39	Aurine carboxylic acid	4-oxypthalein acid and phenol	Pink	542	18.45	-0.4	Increase instead of diminution.

PA = phthalic anhydride TBP = tetrabromophthalic anhydride. BBA = o -benzoylbenzoic acid. ABA = anisoylbenzoic acid.

TABLE II.

Spectra of Derivatives of Fluoresceine (2-2'-oxo-phenolphthalein).

No.	Name.	Source.	Centre of Absorption Band λ .	Frequency.	Diminution of Frequency.	Cause of Diminution.
1	Fluoresceine	PA and resorcinol	499	20.05	—	—
2	3-oxyfluoresceine	3-oxy PA and resorcinol	489	20.45	-0.40	Increase due to 3-oxy group in phthalic ring.
3	Quinolphthalein	PA and quinol	493	20.25	-0.20	Increase due to moving of two OH from <i>p</i> to <i>m</i> .
4	Phloroglucin-phthalein	PA and phloroglucinol	497	20.15	-0.10	Constitution unknown.
5	Resorcinbenzeine	Benzoic acid and resorcinol	501	19.95	0.10	Loss of phthalic - CO ₂ Na.
6	Iso-eosine	TBP and resorcinol	503	19.90	0.15	Addition of four Br in phthalic ring.
7	Succinyl resorceine	Succinic acid and resorcinol	504	19.85	0.20	Replacement of  CO ₂ H by -CH ₂ CH ₂ CO ₂ H.
8	Eosine (tetrabromofluorescein)	—	516	19.35	0.70	4 Br (ortho) in phenol rings.
9	Erythrosine (triiodofluorescein)	—	525	19.05	1.00	4 I (ortho) in phenol rings.
10	Galleine (pyrogallolphthalein)	—	About 543	—	—	? Four - OH groups.
11	Diethylrhodamine (neutral)	—	553	18.10	1.95	Two -OH replaced by two NEt ₂ groups.
12	Diethylrhodamine in acid	—	540 and 559	17.90 and 18.50	1.55 and 2.15	Replacement by NHEt ₂ ion and by NHEt ₂ Cl.
13	Galleine (NaOH)	—	560 broad	17.85	About 2.2	? Four - ONa groups.

tives of phenolphthalein, and Table II gives those which possess the fluorane-oxygen linkage. As will be seen from column 4, the alkaline colours of these phthaleins cover every possible shade due to absorption of light, from the centre of the spectrum to the infra-red, which, from the practical point of view, is very important, since the order of efficiency of the different substituents is probably the same for many other classes of dyes, from which the colour of many unknown dyes could be predicted; at all

events, a similar order appears to reign among the other classes of dyes which have been similarly investigated.

The following are some of the deductions from these observations :

(1) The weight of the substituting material is of little importance compared with its volume; thus the addition of 8 bromine atoms has not much more effect than the addition of 2 *o*-methoxyl groups, and 4 iodine atoms have the same effect as 2 hydroxyl groups. This agrees with the usually accepted view that the atomic volumes of bromine and iodine are not much greater than that of hydrogen, whilst those of carbon, nitrogen, and oxygen are larger.

(2) The position of the substituting group, whether ortho- or meta- to the phenolic hydroxyls, is important; thus the meta-position has more than twice the effect of the ortho-position; in addition, it may be noted that groups actually attached to a phenolic hydroxyl have very little effect.

(3) The two first conclusions may be put in one by supposing that the shifting effect of substituting groups on the absorption-band of phenolphthalein is essentially due to mutual interference of the two phenol rings; such groups as project much from the ring, or are nearer to the junction (the central carbon atom), cause a great effect—an effect which is heightened when the group is unsaturated as in naphtholphthalein, the explanation being that the unsaturated ring is more rigid and causes greater interference to rotation than any combination of simply attached groups could do.

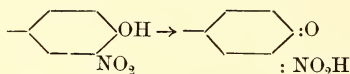
(4) Groups in the phthalic ring have comparatively little effect, which is also the case with acidic groups in the phenolic rings.

(5) Methoxyl groups have a remarkably large effect. This suggests that the oxygen atom is comparatively large in volume, and seems to support the notion suggested by the author in 1906 that oxygen is CX_2 where X is the unknown element (? halogen) of atomic weight 2.

(6) The differences for the same substituent are not always similar—for example, in the different bromo-derivatives—a fact which seems to suggest that there is a mutual action between the groups themselves tending to distort the quinonoid ring which is the cause of the colour. Thus it is striking that the isomeric dibromothymol-, and dibromocarvacrol-phthaleins have almost the same spectrum, whereas there is a slight difference between thymol- and carvacrol-phthaleins lying in the opposite direction.

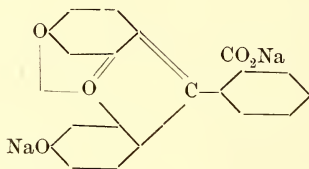
(7) The effect of the bridge oxygen in fluorescein and its derivatives is profound, and must be ascribed to the prevention of rotation of the phenol rings. Contrary to expectation, however, the frequency of the absorption-band is raised—viz. from 18.05 to 20.05—in passing from phenolphthalein to fluorescein, whereas the usual effect of mere loading of a molecule is to lower the frequency, as seen in the 39 derivatives of phenolphthalein described in Table I. It is probable, therefore, that the case of fluorescein is similar to that of the exception in the phenolphthalein series—viz. its

nitro-compound—in that the 2·2'-oxo group distinguishing fluorescein from phenolphthalein must take part in a quinonoid change which totally alters the configuration of the molecule, just as the quinonoid change

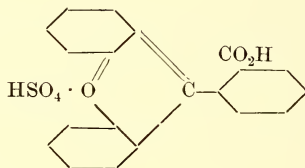


has completely altered the nature of dinitrophenolphthalein.

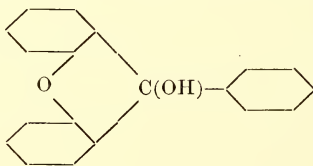
Now, the only orthoquinonoid configuration which can be planned for fluorescein is



in which a phenolic acid group has combined with a basic oxonium group. It should be noted that alternative methods of making this linkage are excluded by the fact that resorcin-benzeine, which is fluorescein minus the CO_2H group, shows the same behaviour as fluorescein, and that fluorane in strong H_2SO_4 shows a similar colour and fluorescence which, I suggest, is due to the linkage



If the still simpler substance of the annexed constitution



could be prepared, its behaviour in H_2SO_4 would, to some extent, settle the question of the cause of the colour and fluorescence of this class of substances.

PHTHALEINS DISSOLVED IN CONCENTRATED SULPHURIC ACID.

The author has discovered that the phthaleins and aurines when dissolved in H_2SO_4 all give coloured solutions with definite absorption-bands.

TABLE III.

Spectra and Colours of Phthaleins in conc. H₂SO₄ Solution.

A. Phthaleins: constant 4.55.

No.	Name.	Frequency in Alkali = <i>x</i> .	Frequency in H ₂ SO ₄ observed = <i>y</i> .	Colour.	Calculated Value of <i>y</i> .
1	Phenolphthalein .	18.05	20.20	Salmon-yellow	20.25
2	Phenolphthalein methylether	18.00	20.05	"	20.18
3	4-oxyphenolphthalein .	18.45	20.80	"	20.85
4	Phenoltetrabromophthalein	17.70	19.95	"	19.73
5	O-cresolphthalein .	17.50	19.65	Pink	19.43
6	Dibromo-o-cresolphthalein	17.30	18.85	"	19.13
7	Tetrabromophenolphthalein	17.15	18.90	"	18.90
8	Thymolphthalein .	16.75	18.25	Purplish-pink	18.30
9	Carvacrolphthalein .	16.65	18.05	"	18.15
10	Octobromophenolphthalein	16.45	17.95	Purple	17.85
11	Thymoltetrabromophthalein	16.05	17.40	Bluish-purple	17.25
12	α -naphtholphthalein .	15.10	15.80	Bluish-green	15.82
13	α -naphtholtetrabromophthalein	14.75	15.30	Green	15.30

B. Fluoresceins: constant 4.7.

1	3-oxyfluorescein .	20.45	23.8	Yellow	23.6
2	Phloroglucinphthalein	20.15	23.1	"	23.2
3	Fluorescein .	20.05	23.2	"	23.0
4	Resorcinbenzeine .	19.95	22.6	"	22.9
5	Iso eosine .	19.90	22.8	Yellowish-salmon	22.8
6	Eosine .	19.35	21.9	"	22.0
7	Erythrosine .	19.05	21.35	"	21.5
8	Galleine .	18.4	21.5	"	20.6

C. Some other Fuchstone-derivatives which do not follow the above law.

A.	Aurine .	18.90	20.8	Salmon	—
B.	Benzaurine .	17.55	21.7	Yellow-salmon	—
C.	Diethylrhodamine .	18.10	21.8	"	—
D.	Quinolphthalein .	20.25	20.1	Salmon	—
E.	Resorcinolphenylphthalein	Violet only	20.25	"	—

The absorption bands in H₂SO₄ of the following substances are: Fluorane, 20.05; fuchstone, 22.0; benzophenone, 21.7; benz-naphthaurine and its -CO₂H derivative (from BBA and naphthol), both 17.6.

and, what is remarkable, that the intensity of the colour is about five times as great as when they are dissolved in alkali. The colours obtained in the two cases are *not* identical; thus, all the phthaleins giving a blue colour in alkali give a pink colour in H₂SO₄. In addition, many other substances of

the fuchsone family can be investigated in H_2SO_4 solution which are not soluble in alkali—*e.g.* fluorane. Table III gives some of the observed results.

The author has been able to trace the very simple law which governs the depression of the colour by H_2SO_4 as compared with alkali. The expression $y = \frac{3}{2}(x - 4.55)$, in which x is the frequency corresponding to alkali solution and y is the frequency corresponding to H_2SO_4 solution for the same phthalein, is found to fit all the direct derivatives of phenolphthalein, and, with the trifling modification to $y = \frac{3}{2}(x - 4.7)$, also fits the whole of the fluorescein series. This means that when the values for y and x actually observed are plotted against one another in the case of all the 50 phthaleins and fluoresceins, all the 50 dots lie approximately on one line. The fact that the quotient is $\frac{3}{2}$ seems to indicate that, as the vibration is $1\frac{1}{2}$ times as fast in H_2SO_4 , there must be three phenyl rings vibrating in H_2SO_4 solution as against two only in alkaline solution. Extraordinary as this may seem, there appears to be no other possible explanation of the raising of the frequency by loading with H_2SO_4 .

It is, however, just possible that the bands in H_2SO_4 are not the bands of alkaline solution raised in frequency, but are secondary bands (originally in the ultra-violet) lowered in frequency by loading with H_2SO_4 . Such secondary bands in alkaline solution, if they exist, would probably have either one-half or one-third of the wave-length of the visible bands, so that the above-discovered law of a linear relationship between H_2SO_4 and alkali solutions would still hold true.

The constant 4.55 (or 4.7) probably expresses the effect of the loading with H_2SO_4 , regarded merely as increasing each of the molecular weights by 98.